

SCIENCE FOR GLASS PRODUCTION

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THERMODYNAMIC ANALYSIS OF MELTING, VITRIFICATION, AND CRYSTALLIZATION IN THE SiO₂ SYSTEM

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A not quite traditional approach to the problem of melting and subsequent vitrification of silica melt and to the problem of quartz glass crystallization in heating is discussed. It is demonstrated that the system enthalpy in the vitrification of a SiO₂ melt remains virtually constant up to the solidification of glass. An estimate of the activation energy of quartz glass crystallization is given.

Numerous publications are dedicated to the melting, vitrification, and crystallization processes in the SiO₂ system. However, we should like to point out a number of vague issues with respect to this subject.

It is known that pure silica in the form of trigonal β -quartz in quasistatic heating at a temperature of 573°C undergoes a polymorphic transformation into hexagonal α -quartz with a very insignificant enthalpy of this transformation ($\Delta H_1 = 0.628$ kJ/mole), and α -quartz at a temperature of about 1400°C is transformed into cubic α -cristobalite, also with a small value of the thermal effect ($\Delta H_2 = 0.838$ kJ/mole). The latter has an equilibrium melting point of 1723°C, and ΔH_m is equal, according to difference sources, to 7.704 – 9.210 kJ/mole, although there are doubts with respect to the accuracy of this value [1].

Considering that the values ΔH_1 and ΔH_2 are small (their sum is equal to 1.466 kJ/mole) and in principle do not disagree with the discussion in the present issue, we will hereafter discuss the thermodynamic aspect only of α -cristobalite, silicate melt, and quartz glass.

Line 1 – 2 – 3 in Fig. 1 represents the process of quasistatic (very slow) heating and melting of α -cristobalite in the coordinates of enthalpy increment $\Delta(H_T^0 - H_{298}^0)$ and temperature. The value $\Delta(H_T^0 - H_{298}^0)$ was calculated as follows:

$$\int_{298}^T C_{\alpha\text{-cr}} dT,$$

where $C_{\alpha\text{-cr}}$ is the heat capacity of α -cristobalite [2] expressed by the temperature sequence:

$$C_{\alpha\text{-cr}} = 17.53 + 88.24 \times 10^{-3} T \text{ (J/mole)}.$$

Direct calorimetric measurements of true heat capacity $C_{\alpha\text{-cr}}$ are known up to temperatures of 600 – 700°C, whereas at higher temperatures experimental difficulties arise and the measurement error of $C_{\alpha\text{-cr}}$ significantly increases. However, extrapolation of the experimental data (in the form of the above equation) to a temperature interval above 600 – 700°C (up to the melting temperature) is not unjustified since cristobalite remains a crystalline phase with a constant type of lattice up to 1723°C (although with a growing degree of defects). Therefore, the course of line 1 – 2 is quite reliable,

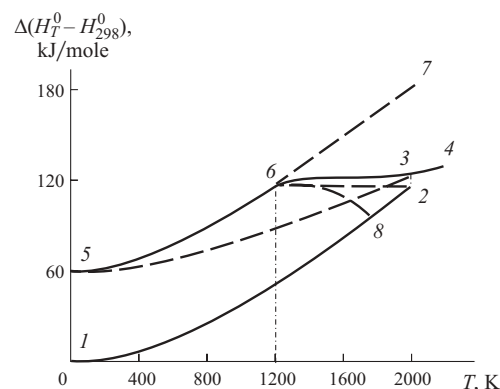


Fig. 1. Variation of enthalpy in the SiO₂ system in heating, melting, vitrification, and crystallization.

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same as the enthalpy increment (ΔH_m) in the transformation of α -cristobalite into a melt (segment 2 – 3).

At a temperature above 1723°C, the SiO_2 melt (line 3 – 4) thermodynamically is an equilibrium phase. Taking into account the energy conservation law, the excess enthalpy of the melt at 1723°C (point 3) will be equal to

$$\begin{aligned}\Delta H_{\text{liq}} &= \Delta(H_{2000}^0 - H_{298}^0)_{\alpha\text{-cr}} + \Delta H_m = \\ 117.7 + 7.704 &= 125.404 \text{ kJ/mole.}\end{aligned}$$

As the melt temperature decreases to 1723°C (about 2000 K), the system receives the possibility of an “alternative” depending on the external conditions (the cooling rate) (point 3 is a kind of bifurcation point). In quasistatic cooling the melt crystallizes in the form of defective α -cristobalite, and the SiO_2 system following the route of 3 – 2 – 1 reverts to its initial state.

In abrupt cooling, the melt rapidly increases its viscosity and solidifies in the form of glass (a metastable nonequilibrium process). Hypothetically it is believed that the enthalpy of the melt and the glass in this case gradually decreases exponentially (curve 3 – 5). The solidified glass has an excess of enthalpy ΔH_g^0 above the enthalpy level of cristobalite.

This statement is generally accepted. It is evident that the specified excess is made up by ΔH_m accumulated in glass in the absence of the crystallization of the melt and by a part of the energy that was spent on rupturing the Si – O – Si chemical bonds in heating the silica to the melting point and did not have time to be released into the ambient medium as heat, because some of these bonds in such rapid cooling did not have time to be restored (reverse overlapping of the valence orbitals of Si and O particles did not happen), i.e., this portion of the energy is determined by the degree of defectiveness of the glass structure ΔH_{def} .

The value ΔH_{def} can be approximately estimated in the following way. According to the contemporary estimates, the number of defects (dislocations or thermal ruptures of Si – O – Si bonds) per surface area of a solid body is of the order of $10^{10} - 10^{13} \text{ cm}^{-2}$ [3]. In particular, the measurements of unit the electrokinetic potential of hydrated particles of extremely pure quartz glass indicate that the density of thermally ruptured Si – O – Si bonds on the quartz glass surface is equal to about 0.8 nm^{-2} [4] or $8 \times 10^{13} \text{ cm}^{-2}$, which correlates with the published data. This is approximately 3% of the total number of Si – O – Si bonds per mole of SiO_2 , and the energy ΔH_{def} in this case is equal to $0.03E_{\text{lat}}$ of SiO_2 , i.e.

$$\Delta H_{\text{def}} = 0.03 \times 1776.5 = 53.28 \text{ kJ/mole.}$$

Accordingly

$$\Delta H_g^0 = 7.704 + 53.28 = 60.984 \text{ kJ/mole,}$$

and taking into account ΔH_1 and ΔH_2

$$\Delta H_g^0 = 60.984 + 1.466 = 62.450 \text{ kJ/mole.}$$

This value in Fig. 1 is equal to about 60 kJ/mole.

By drawing a curve of the temperature dependence of the increment of quartz glass enthalpy $\Delta(H_T^0 - H_{298}^0)$ starting with point 5 and calculated taking into account the equation

$$C_{q,g} = 56.08 + 15.42 \times 10^{-3} T - 14.46 \times 10^5 T^{-2} \text{ (J/mole),}$$

we will obtain line 5 – 6 – 7, that is symbatic with respect to the heating curve of α -cristobalite. The values of $C_{q,g}$ are experimentally substantiated up to a temperature of 600 – 700°C (same as $C_{\alpha\text{-cr}}$ values), and the further course of this curve is the extrapolation of these values to the range of higher temperatures. While quartz glass remains a solid body (its silicon-oxygen lattices is “frozen” in space), the curves $(\Delta H_T^0 - H_{298}^0)_{\alpha\text{-cr}} = f(T)$ and $(\Delta H_T^0 - H_{298}^0)_{\alpha\text{-q,g}} = f(T)$ separated by the value ΔH_g^0 nearly copy each other. This is not surprising, as the chemical composition and strength of Si – O – Si bonds in these materials are virtually the same, and only a greater degree of defectiveness of the disordered polymeric silicon-oxygen glass lattice distinguishes it from the polymeric structure of cubic α -cristobalite.

However, the extrapolation of the course of the curve $(\Delta H_T^0 - H_{298}^0)_{\alpha\text{-q,g}} = f(T)$ to a higher temperature range (segment 6 – 7) results in contradictions. The value ΔH_{liq} at 1723°C (about 2000 K) is 125.404 kJ/mole, whereas this value in curve 6 – 7 is equal to 181.500 kJ/mole. Somehow quartz glass heated to a temperature of 1723°C accumulates an additional energy excess equal to $181.5 - 125.4 = 56.1 \text{ kJ/mole}$ and then for some incomprehensible reason has to “drop” this excess in order to become a normal SiO_2 melt.

The way out of this contradiction can be found as follows. Let us draw an imaginary line from point 2 parallel to the temperature axis up to its intersection with the curve $(\Delta H_T^0 - H_{298}^0)_{\alpha\text{-q,g}} = f(T)$ at point 6. It follows from Fig. 1 that having an initial enthalpy excess ΔH_g^0 , quartz glass heated to a temperature of about 927°C (1200 K) acquires an enthalpy equal to the enthalpy of α -cristobalite at the beginning of its melting at a temperature of 1723°C (2000 K). This means that the level of thermal mobility of the structural elements of the vitreous lattice (the kinetic factor) at 927°C is the same as the level of mobility for α -cristobalite at 1723°C; α -cristobalite melts at this temperature, and the SiO_2 melt is capable of crystallization. Consequently, quartz glass as an unstable thermodynamic phase (a supercooled melt) in theory is also capable of crystallization at the temperature of 927°C (1200 K). In fact after quartz glass is exposed for hundreds of hours at high temperatures exceeding 900°C, the formation of very fine α -cristobalite crystals with a defective structure is observed on its surface [1].

Thus, the value

$$\Delta(H_T^0 - H_{298}^0)_{q.g.} = \int_{298}^{1200} C_{q.g.} dT = (117.7 - 60) = 57.7 \text{ kJ/mole}$$

can be regarded as the activation energy of the process of crystallization of quartz glass under a very slow temperature increase, and point 6 can be regarded as a bifurcation point in heating amorphous silica.

Indeed, quartz glass in the course of very slow heating at temperatures above 927°C will very slowly start crystallizing, releasing the excess of enthalpy into the ambient medium and forming α -cristobalite with a defective structure (line 6 – 8). The quantity of energy released will depend on the quartz glass heating rate, which will be reflected in the position of point 8 on curve 1 – 2. This reasoning does not contradict the experimental data but agrees with them.

Under a relatively fast heating, quartz glass “selects” another alternative. The excessive enthalpy of quartz glass at point 6 (927°C) is equal to 117.7 kJ/mole, and the enthalpy of SiO₂ melt at 1723°C should be 125.404 kJ/mole. Consequently, when heated from 927 to 1723°C, the amorphous SiO₂ system should receive additionally only 7.707 kJ/mole (ΔH_m), which means a slow, extended in time, and nearly isoenthalpic process of transformation of quartz glass into a melt (softening): line 6 – 3. Similarly, in the cooling of the melt (line 3 – 6), the process of transformation of the melt into an amorphous solid body (vitrification), a process very extended in temperature and nearly isoenthalpic, takes place. Depending on the cooling rate, line 3 – 6 can be located slightly above or slightly below the line indicated in Fig. 1, but the general direction of the vitrification process is little affected by these changes. Such reasoning contradicts the existing hypothetical scheme of the transformation of SiO₂ melt into glass (line 3 – 5), but agrees with the experimental facts. The following arguments can be put forward to substantiate this concept.

It is generally accepted that there is excessive enthalpy in glass ΔH_g^0 compared with a crystal. This excess is estimated at about 60 kJ/mole and can be further refined, but a calculation starting from this point $\Delta(H_T^0 - H_{298}^0)_{\alpha-q.g.}$ provides for a thermodynamic determination of the initial crystallization temperature for quartz glass, which agrees with the experimental data, and determination of the activation energy of this process E_{act} .

Having different starting points for calculations ($\Delta H_T^0 - H_{298}^0$), α -cristobalite and quartz glass demonstrate a symbatic course in the dependences $\Delta(H_T^0 - H_{298}^0) = f(T)$ as long as quartz glass is within the range of the proper solid state (its lattice is “fixed” in space). This confirms the known statement that α -cristobalite and quartz glass resemble each other not only in their chemical compositions but in a number of other properties (density, heat capacity).

The traditional hypothetical vitrification scheme (line 3 – 5) assumes that the lower the temperature, the greater the difference between the enthalpy of quartz glass and α -cristobalite for the respective temperature. The largest difference (about 60 kJ/mole) is observed at the end of quartz glass cooling, although the kinetic mechanism of such increase in ΔH_g is not clear. According to the proposed vitrification scheme (line 3 – 6), a difference in the enthalpy equal to ΔH_m exists between the SiO₂ melt and α -cristobalite at the temperature 1723°C. In the case of abrupt cooling, this portion of the energy spent on the transfer of the defective α -cristobalite lattice into the amorphous lattice of SiO₂ melt is accumulated in the system and preserved in it, due to the absence of the reverse crystallization process. When the melt is rapidly cooled, the defects of its silicon-oxygen lattice (thermally broken Si – O – Si bonds) have no time to “heal,” and their number in the solidifying melt up to point 6 will increasingly surpass the number of similar defects in α -cristobalite for the respective temperature.

Thus, the main excess of ΔH_g is formed under high temperatures, and when the quartz glass structure is “frozen” (in final solidification), this excess becomes fixed and preserves its value up to cooling to room temperatures. Such a mechanism of ΔH_g^0 formation is physically more probable.

An objection to the proposed vitrification scheme could be made on the ground that in this case the SiO₂ system over a rather wide temperature interval exists in a nearly isoenthalpy state, although the temperature in the system keeps decreasing. However, these doubts should be dropped considering that the temperature of the system is determined not by its total enthalpy level but by the kinetic energy level ΔH_{kin} of the structural elements comprising the system. The potential part of the energy of a system has no effect on its temperature. Thus, α -cristobalite at point 2 and the SiO₂ melt at point 3 have different levels of ΔH , but their temperature is the same. Glass at point 5 and α -cristobalite at point 1 have the same temperature, but different values of ΔH (and this difference persists at all temperatures as long as glass is within the solid state interval). Consequently, if the total increment of enthalpy of quartz glass transforming into a melt is expressed by curve 5 – 6 – 3, the dependence $\Delta H_{kin} = f(T)$ will resemble curve 5 – 3 in shape and be located below curve 5 – 6 – 3. Apparently, this (not at all evident) curve is the basis of the traditional hypothetical line for the vitrification of high-viscosity melts.

Accordingly, when a high-viscosity SiO₂ melt cools from a temperature of 1723°C, two ways of its transition to a solid state are possible (a bifurcation):

- crystallization at a constant temperature but with decreasing enthalpy in the case of very slow (quasistatic) cooling
- vitrification within a wide temperature interval with a slight variation in enthalpy in the case of abrupt cooling.

Evidently, the lower the ΔH_m value of a material, the more extended is the temperature interval of vitrification (solidifying) or softening (concealed “melting”) of this material.

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